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TO: Dr. D. Mills
Director of Research

TRIP REPORT: 1989 CRYOGENIC ENGINEERING CONFERENCE/ INTERNATIONAL CRYOGENIC MATERIALS CONFERENCE UCLA, LOS ANGELES, CALIFORNIA, JULY 24 - 28, 1989

Jeffrey R. Robins

The 1989 CEC/ICMC conference focused a great deal of attention on flux pinning in high temperature superconductors and on the impact this phenomenon has on critical current density. Material problems appear to be limiting and retarding the growth of uses for high-T_c superconductors. The conference also saw the announcement of the first G-M refrigerator to liquify helium.

INTRODUCTION

The University of California, Los Angeles was the host for the 1989 Cryogenic Engineering Conference/International Cryogenic Materials Conference plus a one-day special Symposium on Critical Current Densities in High-T_c Superconductors. The subjects covered included conventional and high temperature superconductors, low temperature engineering and materials handling, aerospace cryogenics, closed-cycle cryogenic refrigerators, and cryogenic insulation. A major equipment show is also associated with the conference.

The 1989 CEC/ICMC attracted 790 participants from 19 countries. The most noticeable absence was the Peoples Republic of China. A large number of papers were presented from the USSR on superconducting magnetic energy storage systems (conventional superconducting materials).

These conferences are held every 2 years. The last one, in 1987 at Fermi Labs was held shortly after the discovery of high temperature superconductors. The 1987 conference's sessions were actually arranged before the news of these materials broke and thus the new materials were included in a special session. That year the high-T_c materials created tremendous excitement. A large number of presentations were made about new material combinations with higher and higher transition temperatures. There were many predictions of new uses just around the corner. In 1989 the excitement has cooled somewhat, although the materials still hold a large segment of the scientific program. I didn't see one paper on new material combinations or higher transition temperatures.

The focus this year was on understanding the physics of well established high-T_c materials. Studies are concentrating on how to improve their fundamental properties (eg. the special Symposium on critical current densities). A more cautious atmosphere prevailed about the prospects for applications of these materials as their limitations are better understood. In addition there has been an overall increase in work on more conventional superconducting materials and especially in the area of refrigeration.

In 1987 another major topic of interest was the Superconducting Super Collider (SSC). The site for its construction was about to be announced. With Texas now chosen for this project the SSC has faded more into the background as it gets geared up for the actual construction.

This year's conference spent a lot of time on the National Aerospace Plane. This is an ambitious project to design and build a liquid hydrogen fuelled plane capable of achieving orbit after a conventional take off from an airfield. It will travel at Mach 25. One of the challenges of this plane (and there are many) is to develop an aircraft skin capable of having -250°C (liquid hydrogen) on the inside and 1000°C (from air friction) on the outside.

The four plenary sessions outlined some of the main areas of interest:

1. "Prospects and Problems of High-T_c Superconductor Large Scale Applications"
   A. DasGupta, DOE, Washington.

2. "National Aerospace Plane Program: Cryogenic Challenges for the 1990s"
   R.R. Barthelemy, NASP Joint Program Office, WPARB.

3. "Large Magnet Systems with Stringent Superconductor Requirements"
   C. Taylor, Lawrence Berkeley Laboratory.

4. "Fifty Years of Superfluid Helium"
   W.F. Vinen, University of Birmingham, England.

A list of future meetings on cryogenics and superconductivity is given in Appendix II. Appendix III lists manufacturers contacted at the equipment show. The conference program, abstracts and list of attendees are also available.

HIGH TEMPERATURE SUPERCONDUCTORS/ SYMPOSIUM ON CRITICAL CURRENT DENSITIES

Dr. DasGupta of the Department of Energy, in his plenary session outlined the 3 major problems of the new high-T_c superconductors:

- mechanical
- electrical
- chemical

Mechanical problems centre around low fracture toughness and a low tensile strength because grain sizes are limited to 1 - 4 μm. Electrical problems centre on the fact that the critical current density is low. However, in his view the single most crucial problem is the poor chemical stability of these materials both internally and externally.

Research into the new superconductors is moving along three independent tracks; bulk materials, thin films and micro filaments. Dr. DasGupta felt all of the previously proposed applications should have their time scales for development greatly pushed back.

A review of wire manufacturing considerations by Gregory Yurek of American Semiconductor Corporation highlighted a similar set of problems.

There are 4 major areas that concern Mr. Yurek as a wire manufacturer trying to use these new materials:

1. electrical requirements - current densities are too low;

2. mechanical requirements - during manufacture, installation and service. There are questions of uniformity of structure and composition; grain boundaries, the effects of thermal cycling; fracture toughness; maximum continuous lengths; and maximum possible bend radius.

3. The difficulty of processing into useful shapes.

4. Systems issues - such as connections and joints, environmental stability and insulation.

Wire from these materials has been made in a number of ways:

- powder in a tube - ceramic materials in a metal tube heated up and then drawn out into wire. A 100 μm wire has been made to carry $\approx 10^4$ A/cm^2. This technique is fairly good for homogeneity of microstructure and composition and is robust method of manufacture. However, most experiments have been on a few centimetres of wire and what will happen when many meters of wire are manufactured?

- fibre spinning - the production of fibres of the superconducting material that are subsequently embedded in plasticizer and binders. One interesting method of producing these fibres involves producing a molten sphere of the material which you essentially "splatter" to produce the fibres. These methods have problems with homogeneity and crystal alignment and may not be robust during their manufacture.

- Metallic precursors - alloys of the metallic constituents are reacted with oxygen gas. This involves completely reacting the materials with oxygen, not the production of thin films. The final product is very dense. Noble metals such as silver and gold are added to the alloy. These don't oxidize and form conductive islands in the structure.

The Symposium on Critical Current Densities in High-T_c Superconductors spent a full day discussing these new materials and the effects of the microstructure of these ceramics on flux pinning (see Appendix I for a brief description of flux pinning in superconductors). The critical current densities presently possible in these materials are not high. Unlike properties such as the critical temperature, T_c, and the critical field, H_c, the critical current density, J_c, is not a fixed parameter of the material but is extremely sensitive to the microstructure of the sample and its history.

One of the problems highlighted is flux creep (localized flux motion spontaneously generated by thermal activation). This phenomena is more of a problem at liquid nitrogen temperatures since thermal disorder is more severe. Because of the nature of these ceramics there are large numbers of grain boundaries where impurities and non-superconducting material collects. The coupling between this granular material, described as anisotropic grains of stoichiometric material separated by layers of nonstoichiometric material, is being modelled by some workers as arrays of Josephson junctions. A large amount of work is being done in the area of scanning transmission electron microscopy to look at grain boundaries. These studies show that the atomic structure is maintained up to the grain boundary and then the composition changes. Often the grain boundary region is copper rich or the copper and yttrium concentrations oscillate.

CRYOGENIC REFRIGERATION/CRYOGENIC ENGINEERING

A number of new refrigeration systems were presented at this conference. The one to cause the most interest was the development by a Japanese firm of a Gifford-McMahon refrigerator that could achieve liquid helium temperatures in two stages without a Joule-Thomson expansion. They announced the first time that helium had been liquified by such a machine. The advantages of such a refrigerator are simplicity, increased cooling power in a closed-cycle and the removal of the J-T stage which frequently plugs up and requires special sources of very clean compressed helium. These refrigerators do not differ significantly from the one at Research Division (they were commercial refrigerators from CVI). Until now a G-M refrigerator could only go down to approximately 10 - 15K before its cooling capacity vanished. This is caused by the materials used in the regenerators. The regenerator is usually packed with lead spheres. The heat capacity of lead goes to almost zero at 10K and the regenerator stops working. The Japanese have replaced lead with a series of rare earth compounds. The materials used were $Gd_xEr_{(1-x)}Rh$, $Er_{0.5}Dy_{0.5}Ni_2$ and Er_3Ni. The most successful of these was Er_3Ni. This material has a peak in its specific heat curve below 10K. The Japanese have developed a relatively simple technology to form Er_3Ni into spherical particles between 100 and 400 μm. Their 2-stage machine produced 1W at 6.6K. Commercial interest in this new material was high and it is expected to be on the market next year.

Other developments in refrigeration centre around increasing the reliability and time between service for closed-cycle refrigerators. This research is important to space based applications of refrigeration. Increased reliability can be achieved by a series of changes. These include in order of their effectiveness: reducing operating speed; improving rubbing seals; replacing rubbing seals with clearance seals; or finally the elimination of moving parts. One of the better known refrigerators, the Oxford Cryocooler, is being developed as a linear Stirling engine with clearance seals. Clearance seals are used in the compressor and the displacer with no lubrication and no rubbing contact. The Oxford University group developing this unit expect a service life of 5 to 10 years without degradation. In the area of actually eliminating moving parts a lot of development is going into pulse tube refrigerators. These are modified Stirling engines where moving parts have been replaced by changes in pressure in a gas column or with mass surges of a gas through an orifice. Pulse tube refrigerators are still in the development stages; in 1967 the basic system was developed by Gifford with the lowest temperature generated being 125K; in 1984 the use of an orifice extended the temperature to 105K; two stage systems can now get down to 26K. These refrigerators are very reliable and produce no vibration. However, they are currently best built in large sizes.

In the area of cryogenic materials a large amount of work is now being done on hyperconducting aluminum. Hyperconducting aluminum is high purity aluminum in a high strength aluminum matrix cooled to liquid hydrogen temperatures. Cooling ordinary aluminum to LN_2 temperatures produces a factor of 6 drop in its resistivity. However, no further improvements occur as the temperature drops. Hyperconducting aluminum's resistance continues to drop until the temperature approaches 20K. It is lighter than most superconductors and its cooling requirements are less stringent. It has been used for energy storage pulse transformers, storing energy at 10 to 50 kA and delivering power to the load at 1MA or more. These are currently being developed for rail guns, which require power sources that deliver a few megawatts to a few gigawatts for a few microseconds to milliseconds. Electrical generators have also been designed and developed using these materials.

CONCLUSION

This year's meeting reflected the change in direction research into high temperature superconductors is going through. More of the fundamental physics of these materials needs to be understood. A large amount of work will be required in the area of the microstructure of these materials and how this effects the critical current density.

Closed-cycle cryogenic refrigeration is developing rapidly. Lower temperatures, higher powers and greater reliability are the driving forces. It would appear that eventually the use of liquid cryogens will disappear as these refrigerators are further refined.

Approved:

A.F. Baljet
Manager
Electrical Research Department

Submitted:

J.R. Robins
Physical Chemist
Science Section
Electrical Research Department

JRR:JRR:CB

References

1. "Superconductivity - 75th Anniversary" - Special Issue, Physics Today, March 1986.
2. Cryogenic Engineering, edited by B.A. Hands, Academic Press, 1986.
3. Cryogenics, Michael McClintock, Reinhold Publishing, 1964.
4. Solid State Physics, N.W. Ashcroft, N.D. Mirmin, Holt Rinehart and Winston, 1976.

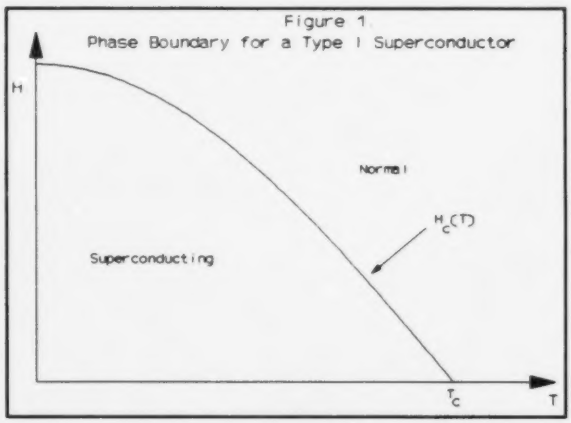
Appendix I

Flux-pinning and Critical Current Density In Conventional Low Temperature Superconductors

The superconducting state is characterized by three parameters: the critical temperature T_c, the critical magnetic field H_c, and the critical current I_c or critical current density J_c. Above T_c superconductors behave as normal metals, at T_c, in the absence of any external magnetic field and with no current flowing, the resistance drops sharply to zero and remains at zero for temperatures below T_c. In addition magnetic flux is excluded from the interior of the superconductor (the Meissner effect). The application of an external magnetic field above a critical value, H_c, will cause reversion to the normal state. This critical field is the point where the energy cost per unit volume of excluding the field exceeds the decrease in free energy of the superconducting state versus the normal.

Superconductors fall into two classes: Type I and Type II. In Type I superconductors below a critical field value there is no penetration of flux, when the applied field exceeds $H_c(T)$ the entire specimen reverts to the normal state. This results in a phase boundary between the superconducting state and the normal state when plotted as field versus temperature (Figure 1.). Typical critical fields in Type I superconductors are about 10^2 gauss.

Figure 1.
Phase Boundary for a Type I Superconductor



In Type II superconductors below a lower critical field H_{c1} there is no penetration of flux in the same manner as Type I superconductors. When the applied field exceeds an upper critical field $H_{c2} > H_{c1}$ the entire specimen reverts to the normal state and the field penetrates perfectly. Between these two fields, the flux exclusion is only partial and the sample develops a rather complicated microscopic structure of both normal and superconducting regions known as a mixed state. It is this phenomenon that makes Type II superconductors useful.

In the mixed state the magnetic field partially penetrates the sample in the form of thin filaments of flux. Within each filament the field is high and the material is not superconducting. Outside the core of the filaments the material remains superconducting. Circulating around each filament

is a vortex of screening current. This results in these filaments often being referred to as flux vortices. Each of these vortices have associated with them a single quanta of flux. In Type II superconductors the upper critical field, H_{c2}, can be as high as 10^5 gauss.

One of the main reasons for the application of superconductivity to electrical machines is that superconductors are capable of handling extremely large currents. Thus the critical current density J_c should be as high as possible. The critical current, I_c, of a Type I superconductor is exactly that current which will produce the critical field at the surface of the conductor. The passage of current through a Type II superconductor in a mixed state causes a different effect.

The interior of a mixed state Type II superconductor, when subjected to a magnetic induction B either applied externally or due to an internal current, is threaded by these quantized magnetic flux vortices. When the superconductor carries a current density J_c, these flux lines experience a force applied to them called a Lorentz force ($F_L = J \times B$ per unit volume). If the vortices are allowed to move around an electric field is generated ($E = v \times B$) where v is the velocity of the flux lines. In order to maintain the zero resistivity of the superconducting state the motion of the flux lines must be stopped. This can be done by the action of a "pinning" force, F_P, acting opposite to the Lorentz force. At equilibrium $F_P + F_L = 0$ and the critical current density J_c is defined as the current density that creates this equilibrium.

But where does this "pinning" force come from? It has its origin in interactions between the flux lines and microstructural features of the superconductor. These microstructural features are regions whose superconducting properties differ from those of the bulk material. They include dislocations and dislocation tangles, grain and twin boundaries, impurities, and precipitates of any second phase. Thus the critical current density, unlike T_c and H_{c2}, is not characteristic of an element, alloy composition or compound, but of a particular sample of material and its history.

A typical Type II superconductor such as the Nb-Ti composite, has two phases. One of which is the superconducting alloy, the other, normal particles of α-Ti less than 5 nm thick. These particles attract the normal cores of the fluxoids and pin them. High densities of these particles, produced by special metallurgical treatments, can produce J_c values as high as 3500 A/mm^2 at 5T.

Instability in a superconductor usually occurs around the critical values where the flux is in a metastable state, the pinning force exactly equalling the Lorentz force. Local flux motion may be generated by thermal activation (flux creep) or the external effect such as sudden changes in current, external magnetic field or mechanical shock (flux jump). This motion causes a local rise in temperature. Since the pinning force usually decreases with increasing temperature a small flux jump can run away and cause a "flux avalanche". This could raise the temperature of the bulk material above the critical temperature and cause the whole superconductor to revert to normal.

All of the above discussion comes from literature on conventional low temperature superconductors. However, the same effects are now being studied in high-T_c materials. Since critical current density depends on flux pinning and the microstructure of the material dictates the pinning force, it can be appreciated how complex this matter is in these ceramic materials with widely differing microstructures.

Appendix II

Future Meetings on Cryogenics and Superconductivity

1. CEC/ICMC 1991 - University of Alabama in Huntsville, Marshall Space Flight Center, June 10 - 14, 1991.

2. 1990 International Industrial Symposium on the Super Collider and Exhibition, Miami Beach, FL, March 14 - 16, 1990.

3. 1990 Applied Superconductivity Conference, Aspen Colorado, September 24 - 28, 1990.

4. Low Temperature Engineering and Cryogenic Conference 1990, Southampton, England, July 17 - 19, 1990.

5. High-Temperature Superconductors - Material Aspects, Garmisch, West Germany, May 9 - 11, 1990.

6. Cryocoolers 6 - International Cryocoolers Conference, Boston, Mass , October 25 - 26, 1990.

Appendix III

Companies Contacted at the Equipment Exhibition

1. American Magnetics	solid state liquid nitrogen level controllers with solid probes of almost any length.
2. Scientific Instruments	cryogenic temperature sensors, digital controllers.
3. Copper & Brass Sales	OFE-HIT copper from Hitachi, ultra high purity, low temperature metals.
4. Lakeshore Cryotronics	cryogenic temperature sensors, temperature controllers.
5. APD Cryogenics	cryogenic refrigerators.
6. Precision Cryogenic Systems	custom engineered cryogenic systems, custom built dewars for liquid helium or liquid nitrogen.
7. Janis	custom cryostats.
8. Cryofab	custom cryostats.
9. Structural Composites Industries	advanced composite materials and structures for use at cryogenic temperatures.
10. Pressure Systems	cryogenic temperature pressure transducers.
11. Quartex	ceramic to metal seals.
12. Provac	quick release flange couplings for vacuum systems, cryogenic valves and fittings.
13. Creare	demountable cryogenic seals for vacuum flanges to replace welded joints.